

Using iron metal rods to infer oxygen status in seasonally saturated soils

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Abstract

The oxygen status in soils is fundamental to a number of earth-science processes including biological, physical and chemical interactions. Since oxygen is time consuming and often difficult to measure in soils, this research explores the use of zero-valent iron rods as a means of estimating oxygen content in soils. Zero-valent iron rods (polished nails) were placed in three soil toposequences and the surface coatings formed by oxidation were compared to measured oxygen concentrations taken every three weeks for one year. When water was present in the soils, the oxygen was measured as dissolved oxygen and in drained conditions it was reported as percent. Coatings on iron metal rods inserted in the soil appear to correlate well with specific oxygen ranges. Rods in soils with O₂ concentrations below about 2 mg l⁻¹ do not develop bright (7.5YR 4/4 to 5/8) oxide/oxyhydroxide coatings, but instead formed black (10YR 2/1–2) coatings. Rods in soils with O₂ concentrations between about 2% to 5% develop variegated bright (7.5YR 4/4 to 5/8) oxide/oxyhydroxide coatings indicating soil drainage and microsite differences in O₂ concentrations. Rods in soils with O₂ concentrations above about 5% with adequate moisture are almost completely coated with bright (7.5YR 4/4 to 5/8) iron oxide/oxyhydroxides. Mineralogy of oxide/oxyhydroxide coatings could not be established by XRD presumably due to the short-range order crystal structure of the metal oxide/oxyhydroxides. This method provides a simple and inexpensive means to qualitatively estimate the ranges of O₂ status in soils. This research may have implications in hydric soil determination, horticultural and agricultural applications, as well as, remediation techniques.

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The oxygen (O₂) status in soils is fundamental to a number of earth-science processes including biological, physical and chemical interactions. The duration, periodicity, and depth of reduction in soil systems influence the emission of greenhouse gases, distribution of plant species, biomass productivity, bioremediation, pedogenic processes, soil corrosivity and placement of soils into aquic and hydric classes.

Anoxic conditions have commonly been related to the presence of free-water in soil. When water fills the pore space, gas is displaced, and the remaining trapped O₂ is utilized during respiration by plant roots, soil fauna and microorganisms. The

biogeochemistry changes once O₂ is depleted from the soil system. Microorganisms utilize other molecules such as NO₃⁻, Mn-oxides, Fe-oxides and sulfates as electron acceptors (Ponnamperuma, 1972).

The change in biogeochemistry is important for soil fertility, soil genesis, plant growth, and microbial degradation. When microorganisms utilize NO₃⁻ as a final electron acceptor, plant available nitrogen can be lost from the soil through denitrification (Simek and Cooper, 2002). During pedogenesis when Fe³⁺ is reduced to Fe²⁺, the Fe becomes soluble and mobile (Ponnamperuma, 1972). This causes iron segregations in areas within the soil observed as iron depletions and concentrations termed redoximorphic features (Vespraskas, 1992). The presence of redoximorphic features is used to infer the presence of a seasonal water table, which relates to soil classification, hydric

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soil determination, septic system filter field design, and soil genesis. The depletion of O_2 also can have a negative effect on plant growth. For most plants, there is very little effect on measured respiration rates observed until oxygen concentrations drop below 5% for whole tissues and 2–3% for tissue slices (Taiz and Zeiger, 1991); however, different plant species have different tolerances to oxygen depletion stress. Only plants such as these with specialized aerenchyma cells, rice for example, are able to transfer O_2 to plant roots allowing them to survive in anoxic soils (Taiz and Zeiger, 1991).

Also related to O_2 concentration in soils and water is bioremediation and chemical remediation. Bioremediation utilizes microorganisms to degrade toxic chemicals to less or non-toxic daughter compounds. Microorganism activity is closely related to O_2 concentration and temperature (Kirschbaum, 1995). Aerobic microbial activity in soil is much higher than anaerobic activity (Moore and Dalva, 1993); therefore, the increased activity results in increased biodegradation of the organic molecule.

Another remediation technique that relates to this study is the use of zero-valent iron metal to reduce compounds such as chromate (Kaplan and Gilmore, 2004; James, 1994) and trichloroethylene (TCE) rendering them non-toxic (Gillham and O'Hannesin, 1994). This remediation technique is commonly used in barriers within aquifers and utilizes the electrons from Fe^0 to reduce the contaminant compounds (USEPA, 1997). If O_2 is present in high enough concentrations, there would be an oxide/oxyhydroxide formed on the surface of the metal, which would increase the Fe^0 , decrease its oxidation rate and render it ineffective.

Oxygen affects many processes in the environment and it is therefore very important to know O_2 activity when making predictions regarding biochemical behavior in a system. Oxygen is commonly measured in the field using polarographic oxygen electrodes, spectrophotometric methods (Rhodazine-DTM), colorimetric methods (indigo carmine) and the Winkler Iodometric titration (APHA, 1998). For field measurements, all of these methods are expensive and time consuming. However, several easily obtainable parameters are measured to infer O_2 status such as Eh, water-table levels, and alpha, alpha dipyridyl reaction. Recently, Indicator of Reduction in Soils (IRIS) tubes have been used to infer anoxic soil environments which lead to iron reduction in soils (Jenkinson and Franzmeier, 2006). There have been limited studies comparing the O_2 concentration found in soils related to the Eh, water-table levels and alpha, alpha, dipyridyl. Both iron rods and IRIS tubes are easy to install and interpret. Iron rods may be most useful in characterizing soil oxidation reactions, and IRIS tubes, in characterizing reduction processes. Installation of both should be very helpful in characterizing soil redox conditions. Like IRIS tubes, inferring O_2 status with iron rods would also provide information regarding microsite redox variability.

Other researchers have tested iron rods as indicators of water-table and plant rooting depths. McKee (1978) proposed using uncoated steel welding rods to measure time-integrated water-table depth. The premise of McKee was that iron forms rust in the oxidized Fe^{3+} state, but is reduced under anaerobic conditions to Fe^{2+} . The boundary between these two conditions

is often approximated by the water table. McKee (1978) found a strong correlation ($r=0.87$) between water-table depth and steel rod rusting depth in several well to poorly drained loamy soils in South Carolina. He recommended installing the rods in the soil for 3 to 4 months during the period of the highest water table. Hook et al. (1987) used the steel rod technique to assess the relationship between red alder (*Alnus rubra*) height and water table. They reported a significant relationship ($r=0.62$) and concluded that the technique was an accurate measure of water-table depth; however, no independent water-table measurements were made.

Carnell and Anderson (1986) measured rusting on steel rods in water, sand, and in a natural soil (Stagnopodzol). They determined that the maximum rust depth correlated well with both water level and rooting depth of Sitka spruce (*Picea sitchensis*). McKee (1978) and Hook et al. (1987) gave few details on criteria for determining the rusting depth; however, Carnell and Anderson (1986) specified the lower level of brown/orange corrosion on the metal correlated with water-table depths.

Bridgham et al. (1991) designed an experiment to determine the suitability of steel rod rusting as a hydrologic indicator in wetland soils, histosols and a mineral soil (Typic Fluvaquents). The study found a good correlation between steel rod rusting depth and water-table depth under both constant and seasonally fluctuating hydrology in Histosols ($r^2=0.80$). In the Typic Fluvaquents, a close relationship between steel rod rusting depth and water-table depth occurred under constant hydrologic conditions. With rapidly dropping water tables rod oxidation showed a lag period behind the response. The technique was deemed unsuitable for wetland delineations due to the prolonged lag periods in rod oxidation under some conditions and the inability of previously formed rust to dissolve upon reflooding.

None of the previous studies related oxygen status of the soil or water to the oxide/oxyhydroxide coatings developed on the iron rods. There were attributes within these studies that suggest a relationship between the presence or absence of oxygen and oxide/oxyhydroxide coatings. Since monitoring oxygen in soils is expensive and time consuming, the purpose of this research was to develop an inexpensive, non-intrusive, simple field technique to infer or estimate the oxygen status in soils.

1. Objectives

The objectives of this research were to test the hypotheses that:

1. Polished, zero-valent iron rods inserted into aerobic soils will develop coatings of iron oxide and oxyhydroxide coatings on the surface of the rods that relate to O_2 concentrations.
2. Polished zero-valent rods inserted into anaerobic soils will remain uncoated.
3. Rod inserted in anaerobic soils with aerobic microsites will develop iron oxide and oxyhydroxide coatings at the aerobic microsites and remain uncoated in zones of anaerobic conditions.

2. Materials and methods

2.1. Site location and monitoring

Multiple soils with different hydrology and textural ranges were needed; therefore, three soil toposequences representing nine soils in the Texas Coast Prairie were monitored and data collected as a reference for developing simple field techniques to measure oxygen content related to iron metal rods (Table 1). The three toposequences were selected because of the range in texture between the three toposequences (Table 2) and the mound–intermound–depression yielded considerable hydrologic differences over relatively short distances. The soil O₂ content, soil redox potential, pH, hydrology, and ferrous iron content were measured; however, only the oxygen data and the iron rod observations are presented in this paper.

2.2. Oxygen concentration related to oxide coatings on rods iron rod experiment

Triplicate, polished low carbon iron metal rods (polished nails) were placed in the soils within 1 meter from the soil water/gas sampling chambers. Thirty-cm long and 0.95 cm diameter low carbon steel rods, which are large nails, (Keystone Wire and Steel Company, Peoria, Illinois) were purchased at a hardware store for use in this research. Analysis of trace elements was conducted analyzed with a Baird model DV-5 optical emission spectrometer and the carbon content of the metal was given as a range of 0.10–0.18% C by weight

Table 1
Classification (Soil Survey Staff, 1998) and landscape position of the soils that were used in this study

Telferner toposequence	
Telferner (mound)	Fine-loamy, siliceous, active, hyperthermic typic albaqualfs
Nada (intermound)	Fine-loamy, siliceous, active, hyperthermic typic albaqualfs
Cieno (depression)	Fine-loamy, siliceous, semiactive, hyperthermic typic endoaqualfs
Gessner toposequence	
Gessner (mound) ^a	Fine-loamy, siliceous, active, thermic oxyaquic paleudalfs
Gessner (intermound) ^a	Coarse-loamy, siliceous, superactive, thermic typic natraqualfs
Gessner (depression)	Fine-loamy, siliceous, active, thermic typic endoaqualfs
Pledger toposequence	
Pledger (upland)	Very fine, smectitic, superactive thermic typic hapluderts
Pledger (transition)	Very fine, smectitic, superactive, thermic typic epiaquerts
Pledger (depression) ^a	Very fine, smectitic, superactive, thermic typic epiaquerts

^a Series names will be given to these toposequence members upon updating of MLRA 150A and 150B but are not available at this time. Gessner mound is currently a taxadjunct of Aris, Gessner Intermound is a taxadjunct of clodine and the tentative name for the Pledger Depression is Chumabog.

Table 2

Texture and percent sand, silt and clay for the soils of the three toposequences

Soil	Depth (cm)	Sand	Silt (%)	Clay	USDA Texture ^a
Gessner (mound)	10	72.1	23.2	4.7	FSL
Gessner (mound)	30	70.5	24.7	4.8	FSL
Gessner (intermound)	10	63.2	31.7	5.1	FSL
Gessner (intermound)	30	48.2	40.0	11.8	L
Gessner (depression)	10	63.0	29.9	7.1	FSL
Gessner (depression)	30	69.3	28.4	7.7	FSL
Telferner (mound)	10	79.6	15.2	5.2	LFS
Telferner (mound)	30	79.6	15.2	5.2	LFS
Nada (intermound)	10	74.1	18.2	7.7	FSL
Nada (intermound)	30	48.3	12.8	38.9	SC
Cieno (depression)	10	47.6	30.2	22.2	SCL
Cieno (depression)	30	51.1	25.7	23.2	SCL
Pledger (upland)	10	1.5	24.7	73.8	C
Pledger (upland)	30	1.1	24.2	74.7	C
Pledger (transition)	10	1.4	23.1	75.5	C
Pledger (transition)	30	1.2	21.3	77.5	C
Pledger (depression)	10	0.6	28.0	71.4	C
Pledger (depression)	30	0.5	26.9	72.6	C

^a FSL = fine sandy loam, L = loam, LFS = loamy fine sand, SC = sandy clay, SCL = sandy clay loam, C = clay.

(Table 3). The exact carbon content of the rods was not given due to proprietary information.

Prior to installation into the soil, the rods were chemically cleaned and physically polished in the lab to remove oily residue and surface coatings. The rods were chemically treated for 1 h 10% HCl solution and then 1 h with 100% ethanol to remove the organic oily coating; then, the rods were physically polished with a wire wheel on a bench grinder to remove other coatings which may prevent oxidation. These polished rods were placed in the soil and removed two weeks later when the depth of water, oxygen content, and soil moisture status were collected. After measurement, a new set of three rods were placed in the soil to be evaluated at the next sampling period. The formation or lack of formation of oxides and oxyhydroxides on the surface of the rod was compared to the oxygen data. A physical description and a photograph were taken of the rods in the field; however, the digital analysis of the rods was not used due to the immediate oxidation of iron upon exposure to atmospheric O₂. The oxide/oxyhydroxide coating was determined by visual inspection with a reference card. The physical appearance of the rod was correlated with chemical and physical data collected for each soil. For each measurement, the depth of water, oxygen content, and soil moisture status were related to the depth of iron oxides/oxyhydroxides.

Table 3

Mean analysis of trace elements of ten rods using a Baird model DV-5 optical emission spectrometer

	Mn (wt.%)	Cr (wt.%)	Co (wt.%)	Ni (wt.%)	Cu (wt.%)	Fe (wt.%)	C ^a
Average	0.38	0.08	NA	0.06	0.22	NA	
Std. dev.	0.02	0.00	NA	0.01	0.02	NA	0.10–0.18

^aRange of values for carbon due to proprietary information.

2.3. Measuring in-situ soil oxygen content

The soil oxygen content was measured by placing a collection chamber in the soil at 10-cm, 30-cm and 50-cm depths (Fig. 1). These collection chambers were constructed using a 3.75-cm PVC pipe with a 0.64-cm hole drilled in the top of the cap. The same size 0.64-cm Cu tubing was placed through the hole and held in place with epoxy (Faulkner et al., 1989). The open end of the cap was covered with geotextile fabric and attached to the PVC cap with epoxy. A hole was bored in the soil of the desired diameter (3.75 cm) and depth (10, 30 and 50 cm); then, the collection chamber was placed in each hole and backfilled with bentonite. The Cu tubing was brought to the surface and capped with an airtight valve to allow access to the collection chambers in the soil at given depths in isolation from the atmosphere. A Nalgene® hand held vacuum pump that had 48 kPag positive pressure at the outlet port was used to draw air/solution into a chamber to sample the liquid and/or gas.

The oxygen content was measured with a YSI Model 610DM Display with a 600 Multi Parameter Probe. This probe simultaneously measured oxygen, temperature, electrical conductivity/salinity, and pH. At times when there was only gas present in macropores, the gaseous oxygen content was determined using the methods described by Patrick (1977); and, when the macropores were filled with water, dissolved oxygen was determined in the liquid phase.

During the field measurement of oxygen (O_2) concentration, the instrument O_2 readings decreased rapidly and remained relatively constant (usually after about 5 min) at which time the O_2 measurements were taken during the period of equilibration (Fig. 2). The steady state dissolved oxygen meter will give similar curves due to depletion of O_2 at the electrode giving an apparent low concentration of O_2 . With a steady state DO probe, the problem can be relieved by continuously stirring the sample. The rapid pulse integrated electrode used for these measurements alleviates this problem by using a pulsed integrated measurement so the O_2 is not depleted at the electrode. This allows for a much more sensitive reading at lower oxygen

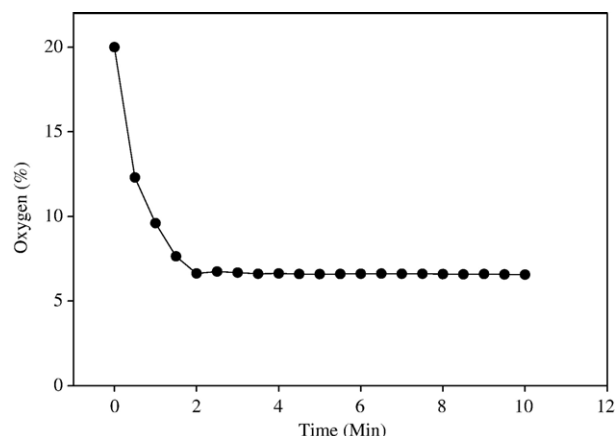


Fig. 2. Graph of oxygen measurement in gaseous phase versus time.

concentrations. In addition, while taking these measurements the gas or liquids were in continuous motion across the electrode, which further decreases the probability of this type of error.

2.4. Soil hydrology

Soil hydrology was measured with piezometers and tensiometers. Piezometers were installed in triplicate at 25-cm, 50-cm, 100-cm and 200-cm depths in the Nada–Cieno–Telferner and the Gessner toposequence (Starowitz, 1994) according to Faulkner et al. (1989). The Pledger toposequence had piezometers at 30 cm depth rather than 25 cm. Also, tensiometers were installed in triplicate at 10-cm, 30-cm and 50-cm depths at each site. Calibration of soil pressure potentials with gravimetric water content allowed prediction of water content from tensiometric pressure potentials.

2.5. Preliminary field study

Prior to installing the Eh electrodes and soil collection chambers, a study was conducted during a wet season comparing piezometer data, alpha, alpha dipyrldyl and the iron rods in one toposequence. This was a 12-week study where rods were placed in the Nada–Cieno–Telferner toposequence and checked every three weeks. Initially, four sets of triplicate iron rods were inserted in the three soils. After checking the triplicate set of iron rods, a new triplicate set of rods were placed in the soil. This would give an indication of the change in surface rod features over 12 weeks and the change within the three-week period.

3. Results

3.1. Preliminary laboratory study

In a greenhouse, polished zero-valent iron rods were placed in a drained sandy loam soil at field capacity (around 10 KPa) to determine the time of oxide formation. Within an hour, bright orange oxides formed on the top of the rods exposed to

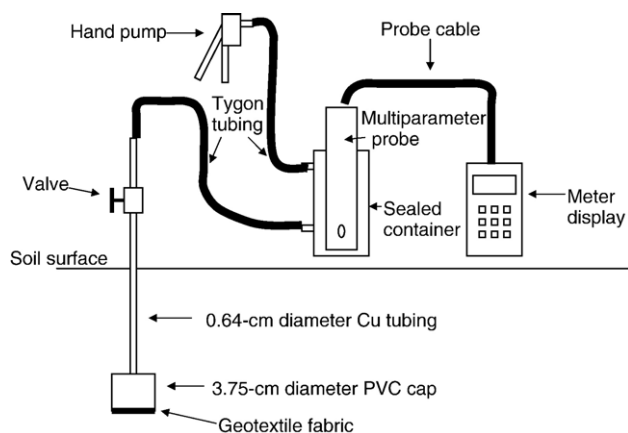


Fig. 1. Illustration of the collection chamber and the soil solution monitoring apparatus.

atmospheric O_2 . This was the top plate of the rod and the rest of the rod was in the soil. Within eight hours, localized bright orange oxides formed on the entire length of the rod. Within three days, the iron rods developed bright orange oxide coatings on both the buried and exposed parts of the rod, with complete coverage of the rod. This study indicated that the iron rods could form easily identifiable oxides within an oxidized soil within one day and form oxide coatings to cover the entire rod after three days.

3.2. Preliminary field study

In the preliminary field study, the lack of iron oxide formation on the rod appeared to correlate well with the positive reaction to alpha, alpha, dipyridyl in a soil with reduced (Fe^{2+}) iron in solution. When the piezometer data indicated no free-water and the alpha, alpha dipyridyl had a negative reaction, there were clearly visible oxide/oxyhydroxide coatings on the iron rods. However, in the transition soil (Nada) where the free-water fluctuated, there were bright orange and red oxides that had formed on the iron rod while the soil was oxidized. Following a large rain event, there was free-water indicated in the piezometers and the soil had a positive reaction to alpha, alpha dipyridyl inferring anoxic conditions. The oxides that had formed on the iron rod during oxic conditions were still visible after saturation and reduction. The appearance of the oxides had changed from bright orange colored oxides to a deep red color. Possibly, some of the oxides/oxyhydroxides are more easily reducible oxides and were reduced and dissolved. According to Fischer (1988) iron oxides reduce at different redox potentials. This article reports that at a pH 7 and a Fe^{2+} concentration of 10^{-4} M, ferrihydrite reduces at 40 mV, lepidocrocite reduces at -160 mV and goethite reduces at -310 mV. Since reduction reactions are endothermic and require energy input by microorganisms to proceed, the reduction reactions are slow and depend on soil properties such as labile carbon (Lovely, 2000). The most easily reducible iron oxides (such as ferrihydrite) may be reduced while other more stable oxides remain in the oxide form. The system may be sufficiently limited by carbon or time to result in complete reduction of the all of the iron oxides. This method utilizes a very concentrated form of iron and depends on a rapid exothermic reaction which is entirely a chemical oxidation that results in the formation of iron oxides. The oxidation reaction may occur in a few minutes (Waseda and Suzuki, 2006) while the reduction process in soils may take weeks (Ponnamperuma, 1972). Compared to the IRIS tubes, the iron oxides on these tubes are of known mineralogy and relatively low concentrations. When reducing conditions are present in the soil, the IRIS tubes reflect the reducing conditions and exhibit stripping of the iron oxides (Jenkinson and Franzmeier, 2006). The most important conclusion to the preliminary study was that oxides/oxyhydroxides formation or lack of formation would indicate aerobic or anaerobic soil conditions; however, once these oxides/oxyhydroxides were formed on the iron rod, they were not easily reduced and removed during subsequent reducing conditions. Thus, the rods can not be used over ex-

tended periods as an integrated estimation of free-water or O_2 in the soil.

3.3. Relationship of oxide coatings to oxygen concentration

For all rods, there was an increasing presence of oxide coatings within ranges of increasing O_2 concentration in aqueous and gaseous phases. The O_2 content in the research site soils during the time of measurement ranged from 0.1 mg l^{-1} – 2.9 mg l^{-1} in soil water and 0.9%–16% in soil air. There were no bright (7.5YR 4/4 to 5/8) iron oxides/oxyhydroxides present on the rods when there was free-water, indicated by piezometer data, within the horizon.

The different soil toposequences gave slightly different ranges and variabilities of O_2 concentration related to percent oxide/oxyhydroxide rod coverage of when compared separately; however there were no significant differences. The different soils will be discussed separately to illustrate the similarities in soil O_2 ranges.

The Gessner soil is a fine sandy loam (Table 2) and has the least amount of clay of the three toposequences. There were no bright coatings on the iron rods when the O_2 concentration in the soil when DO ranged from 0 to about 3.5 mg l^{-1} . Once the

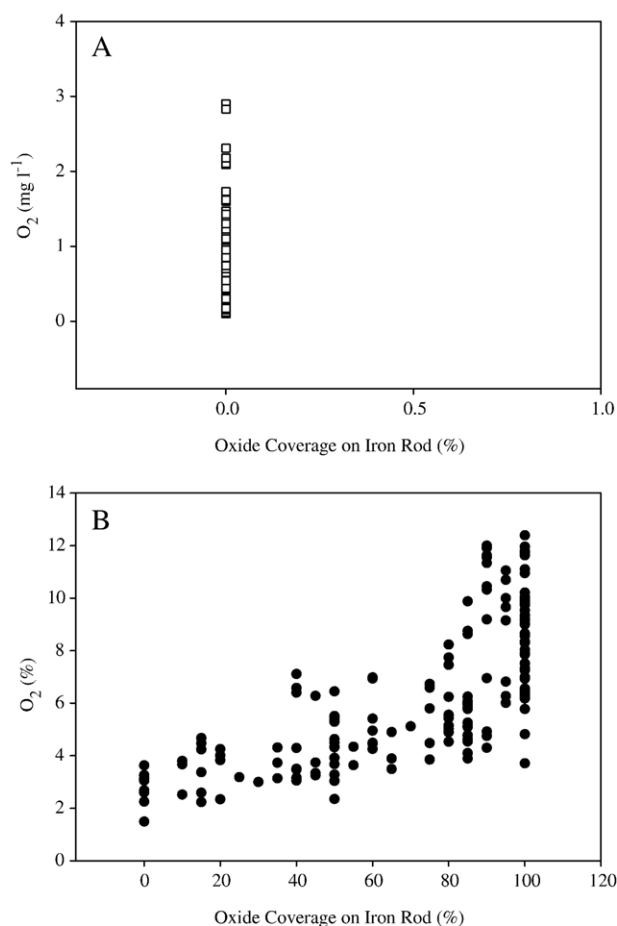


Fig. 3. Relationship of iron oxide/oxyhydroxide coatings to dissolved oxygen concentration on iron metal rods in all soil and all depths (A); and relationship of iron oxide/oxyhydroxide coatings to gaseous oxygen concentration on iron metal rods in all soil and all depths (B).

soil drained and air entered the system, there was a sharp increase in the percent of bright coatings from about 3.5% to 6% soil O_2 showing a strong relationship between the O_2 concentrations and percentage bright coatings on the rod (Fig. 3). These oxide/oxyhydroxides were variegated and commonly in the shapes of roots and/or pores which suggests air entering the macropores subsequent to the removal of water.

The Nada–Cieno–Telferner toposequence is loamy soil and has more clay than the Gessner toposequence but much less than the Pledger toposequence. The relationship of the O_2 in the soil to the percentage oxides/oxyhydroxides on the rods was very similar to the Gessner toposequence. There were no bright coatings when DO concentrations ranged from about 0 to $2.9 \text{ mg l}^{-1} O_2$. Soil air O_2 values near 4% correspond to 20–50% coverage of the iron rod. The iron rods were almost completely coated from about 6% to 12% O_2 in the soil air.

The high clay Pledger toposequence yielded a similar pattern as the previously discussed toposequences with differences in the ranges and variability. There were no bright coatings when DO concentrations ranged from about $0\text{--}2 \text{ mg l}^{-1}$ and a increase in coatings from about 2% to 7% O_2 in the soil air (Fig. 3). The data indicate more variability than the other toposequences with some values around 7% O_2 concentration giving as much as 50% coverage of bright coatings.

Comparing the data of all the toposequences as mean values of O_2 concentration in the soil and percent oxide/oxyhydroxides on the iron rod revealed that when the soil contained free-water and DO was below about 2 mg l^{-1} , there were no bright oxides formed on the rods (Figs. 3 and 4). When the soil was saturated and DO was below about 2 mg l^{-1} , there were black coatings that were magnetic and many have the shape of plant roots or pores (Fig. 4). These coatings were analyzed using X-ray diffraction and the only identifiable peak was siderite ($FeCO_3$). This is probably due to the short-range order crystalline structure of the iron oxide/oxyhydroxide minerals. The magnetic properties of these coatings, suggest a mixed valent iron oxide such as magnetite ($FeFe_2O_4$) or maghemite ($\gamma\text{-}Fe_2O_3$) (Black-

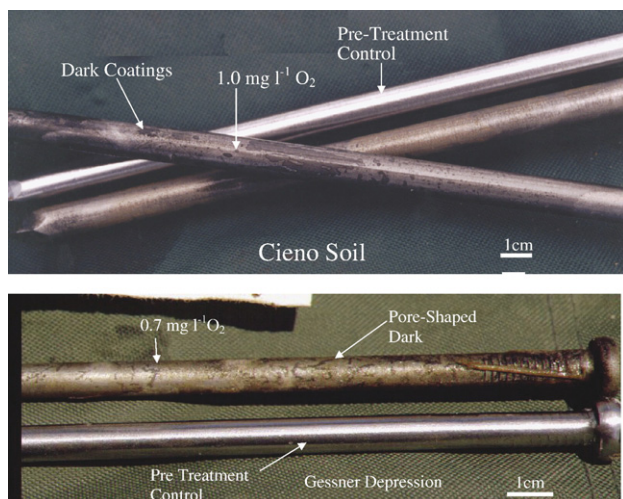


Fig. 4. Iron rods in low oxygen status illustrating the lack of bright coatings and dark pore-shaped coatings.

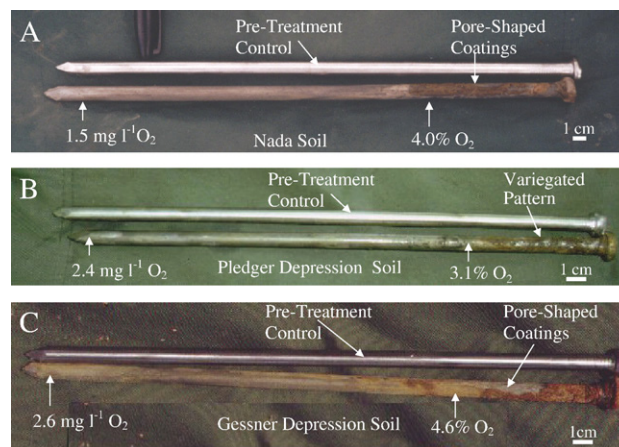


Fig. 5. Iron rods with mixed oxygen concentrations ranging from $0\text{--}2.6 \text{ mg l}^{-1} DO$ and 3.1–4.6% soil air illustrating variegated patterns and pore-shaped bright coatings.

burn and Dennen, 1994); however, there was not an identifiable peak in the XRD pattern. The Fe^0 oxidizes to Fe^{2+} at -440 mV so at Eh's above -440 , there would be a chemical oxidation. Reduced soils rarely have Eh's below -200 mV (Ponnamperuma, 1972) suggesting a high concentration of Fe^{2+} near the surface of the rod.

At a soil air O_2 content ranging from about 2% to 5%, there were variegated patterns with some shaped like soil pores (Fig. 5). The variegated pattern and pore-shaped coatings on the rod are interpreted as macropores filling with O_2 following drainage of free-water. Or in the case of episaturated soils, the gas exchange was decreased by the presence of water filled pores in the overlying horizons and subsequently depleted by microbial respiration. Once the water is evapotranspired or drained, the gas re-enters the pores increasing the O_2 concentration to levels sufficiently high to form bright coatings. The bright coatings ranged from 5 to 100% coverage with a mean of 47% (median 50% and standard deviation of 35%) coatings on the iron rod when soil air O_2 concentrations ranged from 2–5%.

At soil air O_2 contents above about 5%, the iron rods had bright (7.5YR 4/4 to 5/8) coatings covering at least 50% and

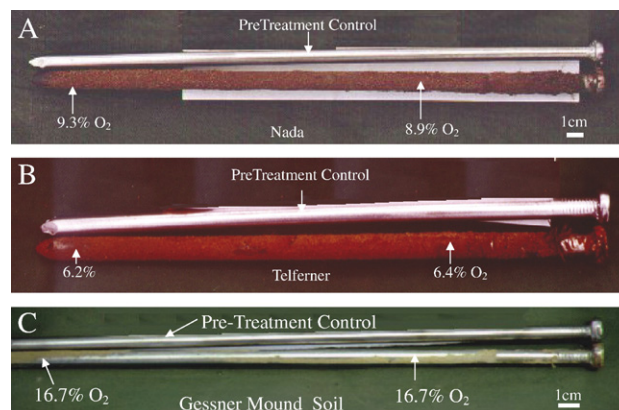


Fig. 6. Iron rods in greater than 6% soil air oxygen concentration illustrating bright coatings (A and B). Iron rod (C) placed in dry soil indicating minimal oxide coatings.

frequently more than 80% of the rod surface (Figs. 5 and 6). At O_2 concentrations ranging from about 5% to 7% the percent of bright coatings ranged from 40% to 100% with a mean of 79% (median of 80% and standard deviation of 20%) coverage of the iron rod. The mean was 98% (median 100% and standard deviation of 4%) coverage of bright coatings on rods in soils with 7–12% O_2 concentration.

During the dry season, O_2 data yielded concentrations above 12% yet the iron rods were coated with 20% to 80% bright coatings (Fig. 6). This suggests that the limited formation of coatings was due to low soil water content; thus, indicating water is necessary for the oxidation reaction (Fig. 6). The 100 KPa ceramic cup on the tensiometers did not allow comparison between the formations of oxide coating on the rod at low moisture content. These rods appeared much different than the low O_2 status rods because the low moisture and high O_2 , rods would remain brightly polished with none of the dull black coatings on the surface.

4. Conclusions

Coatings on iron metal rods (polished nails) inserted in the soil appear to correlate well with specific oxygen ranges. Rods in soils with dissolved O_2 concentrations below about 2 mg l^{-1} do not develop bright (7.5YR 4/4 to 5/8) oxide/oxyhydroxide coatings, but instead form black (10YR 2/1–2) coatings. Rods in soils with O_2 concentrations between about 2% to 5% develop variegated bright (7.5YR 4/4 to 5/8) oxide/oxyhydroxide coatings indicating microsite differences in O_2 concentrations. Rods in moist soils with O_2 concentrations above about 5% almost completely coated with bright (7.5YR 4/4 to 5/8) iron oxide/oxyhydroxides. Mineralogy of oxide/oxyhydroxide coatings could not be positively identified by XRD presumably due to the short-range order crystal structure of the metal oxide/oxyhydroxide. Once iron oxide/oxyhydroxides were formed on the rod, they were not reduced during subsequent reducing conditions. Unlike IRIS tubes, which will provide an integrated assessment of iron reducing conditions over time, these data indicate the iron rods can be used to provide information on a O_2 status over a bracketed time period rather than an integrated measurement. Iron rods and IRIS tubes are easy to install and interpret. Iron rods are most useful in characterizing soil oxidation reactions, and IRIS tubes, in characterizing reduction processes. Installation of both should be very helpful in characterizing soil redox conditions for uses such as hydric soil determination. Since assessment of O_2 concentration is difficult, expensive and time consuming to measure in soils, this method may have applications to qualitatively estimate the ranges of O_2 status in soils. This research may have environmental, horticultural and agricultural applications, as well as, applications in remediation techniques.

References

American Public Health Association (APHA), 1998. Standard methods for the examination of water and wastewater, 20th ed. Am. Public Health Assoc, Washington DC.

- Blackburn, W.H., Dennen, W.H., 1994. Principles of mineralogy. Wm. C. Brown Publishers, Dubuque, IA.
- Bridgman, S.D., Faulkner, S.P., Richardson, C.J., 1991. Steel rod oxidation as a hydrologic indicator in wetland soils. *Soil Sci. Soc. Am. J.* 55, 856–862.
- Carnell, R., Anderson, M.A., 1986. A technique for extensive field measurement of soil anaerobism by rusting on steel rods. *Forestry* 59, 129–140.
- Faulkner, S.P., Patrick, W.H., Gambrell, R.P., 1989. Field techniques for measuring wetland soil parameters. *Soil Sci. Soc. Am. J.* 53, 883–890.
- Fischer, W.R., 1988. Microbiological reactions of iron in soils. In: Stucki, J.W., Goodman, B.A., Schwertmann, U. (Eds.), *Iron in Soils and Clay Minerals*. D. Riedel Publ., Boston, MA.
- Gillham, R.W., O'Hannesin, S., 1994. Development of zero-valent iron as an in situ reactant for remediation of VOC-contaminated groundwater. *Ground Water* 32, 844.
- Hook, D.D., Murray, M.M., DeBell, D.S., Wilson, B.C., 1987. Variation in growth of red alder families in relation to shallow water table levels. *For. Sci.* 33, 224–229.
- James, B.R., 1994. Hexavalent chromium and reduction in alkaline soils enriched with chromite ore processing residue. *J. Environ. Qual.* 23, 227–233.
- Jenkinson, B.J., Franzmeier, D.P., 2006. Development and evaluation of iron-coated tubes that indicate reduction in soils. *Soil Sci. Soc. Am. J.* 70, 183–191.
- Kaplan, D.I., Gilmore, T.J., 2004. Zero-valent iron removal rates of aqueous Cr (VI) measured under flow conditions. *Water Air Soil Pollut.* 155, 21–33.
- Kirschbaum, M.U.F., 1995. The temperature dependence of soil organic matter decomposition, and the effect of global warming on soil organic C storage. *Soil Biol. Biochem.* 27, 753–760.
- Lovely, D.R., 2000. *Fe (III) and Mn(IV) reduction*. ASM Press, Washington, DC.
- McKee Jr., W.H., 1978. Rust on iron rods indicates depth of soil water tables. In: Balmer, W.E. (Ed.), *Soil moisture-site productivity symposium*. Myrtle Beach, SC. 1–3 Nov. 1977. USDA, Washington, DC, pp. 286–291.
- Moore, T.R., Dalva, M., 1993. The influence of temperature and water table position on carbon dioxide and methane emissions from laboratory columns of peatland soils. *J. Soil Sci.* 44, 651–664.
- Patrick Jr., W.H., 1977. Oxygen content of soil air by a field method. *Soil Sci. Soc. Am. Proc.* 41, 651–652.
- Ponnamperuma, F.N., 1972. The chemistry of submerged soils. *Adv. Agron.* 24, 29–96.
- Simek, M., Cooper, J.E., 2002. The influence of soil pH on denitrification: progress towards the understanding of this interaction over the last 50 years. *Eur. J. Soil Sci.* 53, 345–354.
- Starowitz, S.M., 1994. A study of aquic conditions in a microtoposequence of seasonally wet soils on the Texas Coast Prairie. M.S. Thesis. Texas A&M Univ., College Station, TX.
- Taiz, L., Zeiger, E., 1991. *Plant physiology*. Benjamin/Cummings Publishing Company, Inc.
- United States Environmental Protection Agency, 1997. Permeable reactive subsurface barriers for the interception and remediation of chlorinated hydrocarbon and chromium(VI) plumes in groundwater. Office of Research and Development, National Risk Management Research Laboratory, Ada, OK. EPA/600/F-97/008.
- Vesprskas, M.J., 1992. Redoximorphic features for identifying aquic conditions. North Carolina Agricultural Research Service. North Carolina State University. Raleigh, NC. Tech. Bull. 301.
- Waseda, Y., Suzuki, S., 2006. *Characterization of corrosion products on steel surfaces*. Springer Press, New York, NY.